



Electrosynthesis of hydrogen peroxide in acidic solutions by mediated oxygen reduction in a three-phase (aqueous/organic/gaseous) system

Part I: Emulsion structure, electrode kinetics and batch electrolysis

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Abstract

The mediated electrosynthesis of H_2O_2 in acidic solutions (pH 0.9–3.0) was investigated in a three-phase, aqueous/organic/gaseous system using 2-ethyl-9,10-anthraquinone (EtAQ) as mediator (redox catalyst). The main hydrogen peroxide producing route is the *in situ* mediating cycle: EtAQ electroreduction–homogeneous oxidation of anthrahydroquinone (EtAQH₂). The organic phase was composed of tributylphosphate solvent (TBP) with 0.2 M tetrabutylammonium perchlorate (TBAP) supporting electrolyte, 0.06 M tricaprylmethylammonium chloride (A336) surface active agent, and 0.1–0.2 M EtAQ mediator. Part I of this two part work deals with the physico-chemical characteristics of the emulsion electrolyte (e.g., ionic conductivity, emulsion type, H_2O_2 partition between the aqueous and organic phases), and kinetic aspects (both electrode and homogenous) of the mediation cycle. Furthermore, batch electrosynthesis experiments are presented employing reticulated vitreous carbon cathodes (specific surface area $1800 \text{ m}^2 \text{ m}^{-3}$) operated at superficial current densities of $500\text{--}800 \text{ A m}^{-2}$. During 10 h batch electrolysis involving the emulsion mediated system with O_2 purge at 0.1 MPa pressure, H_2O_2 concentrations in the range 0.53–0.61 M were obtained in 0.1 M H_2SO_4 (pH 0.9) and 2 M Na_2SO_4 (acidified to pH 3). The corresponding apparent current efficiencies were from 46 to 68%. Part II of the present work describes investigations using flow-by fixed-bed electrochemical cells with co-current upward three-phase flow.

List of symbols

C	concentration (M)
F	Faradaic constant ($96\,500 \text{ C mol}^{-1}$)
$I_{\text{L,R}}$	limiting current obtained from voltammetry in the case of redox regeneration (A)
$I_{\text{p,c}}$	voltammetric peak current (A)
k_{C}	pseudo first order homogeneous rate constant (s^{-1})
$K_{\text{H}_2\text{O}_2}$	H_2O_2 partition coefficient between the aqueous and organic phases
n	total number of electrons involved in the EtAQ reduction
R	universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
T	temperature (K)
v	scan rate (V s^{-1})

Greek symbols

ε	volume fraction of the organic phase in the emulsion
κ	specific ionic conductivity (S m^{-1})

Abbreviations

A336	Aliquat® 336 (tricaprylmethylammonium chloride)
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DEB	diethylbenzene
EtAQ	2-ethyl-9,10-anthraquinone
ppc	pores per centimetre
RVC	reticulated vitreous carbon
TBAP	tetrabutylammonium perchlorate
TBP	tributylphosphate

1. Introduction

The industrial scale application of the direct two-electron reduction of O_2 is limited to strong alkaline solutions (e.g., 2 M NaOH) yielding peroxide concentrations in the range of 1.0–1.5 M. The alkaline peroxide solution has a niche market for on-site bleaching and/or brightening of diverse wood pulps [1, 2]. Research has been carried out to improve the performance of direct O_2 electroreduction to H_2O_2 , with respect also to lowering the alkalinity of the electrolyte and possibly using neutral or acidic solutions. Under the latter conditions the main challenge is the sluggishness of the two-electron O_2 electroreduction as shown for instance, by about a five order of magnitude smaller standard rate constant for electroreduction in 0.1 M H_2SO_4 as compared to

0.1 M Na_2CO_3 [3]. Consequently, in acidic solutions high current efficiencies for direct O_2 electroreduction (e.g., above 80%) can only be obtained at low, industrially impractical, superficial current densities (e.g., at pH 2 a current efficiency of 81% was obtained using a graphite cathode operated at only 6.4 A m^{-2} [4]).

To increase the rate of two-electron O_2 reduction a variety of approaches have been examined, including electrocatalysis (by transition metal macrocycles [5] or surface bound quinone compounds [6, 7]), homogeneous mediation (using either a water-soluble anthraquinone derivative [8] or water-miscible organic systems with dissolved anthraquinone [9, 10]) and exploitation of interfacial effects induced by cationic surfactant electro-sorption [3]. Generally, there is little information on the applicability of the above methods under conditions and cell designs relevant to industrial scale electrosynthesis of H_2O_2 .

Employing a trickle-bed electrochemical cell with graphite felt cathode of 0.5 m effective length, it was found that the presence of 1 mM concentration of tricaprylmethylammonium chloride, $[\text{CH}_3(\text{CH}_2)_7]_3\text{CH}_3\text{-N}^+\text{Cl}^-$, in 1 M Na_2SO_4 at pH 3, yielded a current efficiency of 39% at 1050 A m^{-2} superficial current density, while under the same conditions but without surfactant present the current efficiency was only 24% [11]. In spite of the marked improvement, for a commercially feasible system a much higher current efficiency is required (>80%).

An alternative to the methods discussed above is the *in situ* emulsion mediated electroreduction of O_2 . In this case, employing a porous electrode, the oxygen gas phase is brought into contact with a L/L electrolyte comprising of an aqueous phase (pH < 7) and an organic solution, which contains dissolved in it an

anthraquinone derivative acting as redox catalyst (Figure 1, Scheme 1).

Hydrogen peroxide, formed in the bulk of the organic phase by the chemical reaction between the reduced form of the redox catalyst (anthrahydroquinone) and oxygen from the gaseous phase, is distributed between the aqueous and organic solutions as a function of the partition coefficient. For convenient downstream processing it is desirable to use a L/L electrolyte with an aqueous/organic H_2O_2 partition coefficient greater than unity. Following separation of phases the peroxide-rich aqueous acidic solution could meet the requirements of industrial processes such as pulp bleaching (e.g., GreenOx[®] process [12]), mineral leaching and organic effluent treatment.

In the multiphase system under consideration, in addition to the mediating cycle, H_2O_2 is also generated by a parallel 'direct' $2e^-$ reduction of O_2 (Figure 1, Reaction 2). Furthermore, the electrogenerated H_2O_2 can undergo electrochemical and/or catalytic decomposition to H_2O , according to the secondary Reactions 3 and 4 shown by Figure 1.

From a fundamental point of view, the main advantage of three-phase redox catalysis lies in the fact that the major peroxide-producing pathway is not aqueous O_2 electroreduction, which is sensitive to electrolyte pH and composition, but chemical oxidation of the anthrahydroquinone derivative in the organic phase. Theoretically, therefore, emulsion mediation offers the potential of H_2O_2 electrosynthesis over a wide range of pH, ideally between 1 and 14.

Tobias and coworkers were the first to report on the emulsion electroreduction of an anthraquinone derivative (i.e., 2-ethyl-9,10-anthraquinone, EtAQ) using a NaOH solution aqueous phase [13]. The goal of their

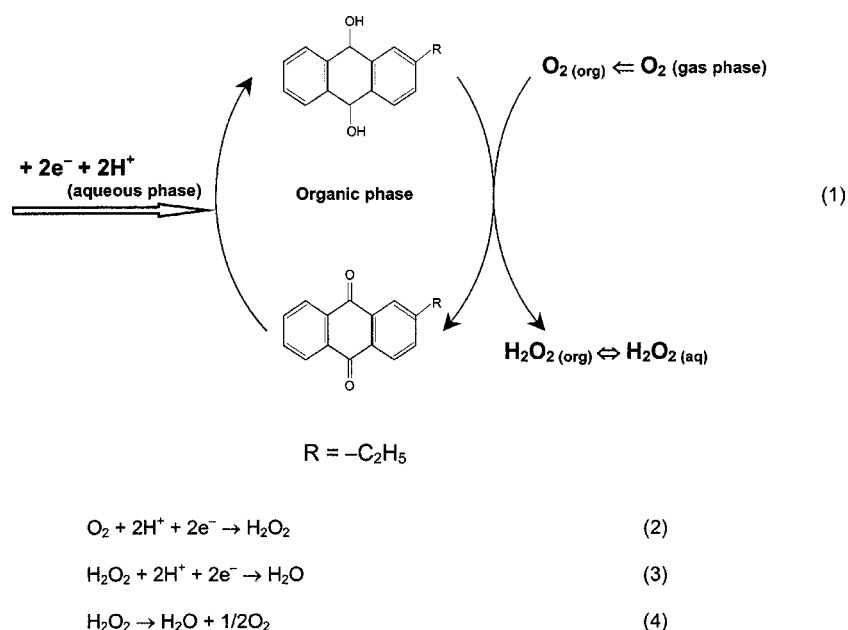


Fig. 1. The principle of mediated H_2O_2 electrosynthesis in a three-phase system.

study was to investigate the feasibility of replacing the catalytic step in the thermochemical anthraquinone process of peroxide production with an electrochemical route. Consequently, these researchers did not aim at the simultaneous, *in situ* generation of H_2O_2 . The proposed emulsion was composed of 1–2 M NaOH aqueous phase (up to 60% by vol.) and an organic phase composed of a diethylbenzene (DEB) and tributylphosphate (TBP) mixture with 0.42 M EtAQ dissolved in it. The cathode was Pb electrodeposited on reticulated vitreous carbon (RVC) [13].

Recently, Huissoud and Tissot investigated the possibility of *in situ* generation of peroxide using the alkaline emulsion proposed by the Tobias group [14, 15]. A peroxide concentration of 0.8 M was obtained in 2 M NaOH, after 6.5 h of continuous catholyte recycle using an 8 pores per cm (20 pores per inch, ppi) RVC cathode operated at 225 A m^{-2} . However, the large-scale applicability of this method for the production of peroxide in 1–2 M NaOH is limited. In the latter electrolyte O_2 is fairly efficiently reduced on a variety of three-dimensional carbon based cathodes by a direct (unmediated) 2e^- electrochemical process [1]. The commercial Dow–Huron process for instance, employs a packed-bed cathode composed of graphite particles coated with a mixture of carbon black and Teflon. Operated at atmospheric pressure, $700\text{--}1500 \text{ A m}^{-2}$, 2.4 V per cell, the Dow–Huron cell produces typically a solution composed of 1.2–1.5 M H_2O_2 in 1.8–2.0 M NaOH with a current efficiency of 85% [16, 17]. Therefore, the emulsion system, introducing potential engineering and operational difficulties, has little merit in the case of peroxide electrosynthesis in strong hydroxide solution.

The goal of the present study was to develop an organic redox catalytic system for H_2O_2 electrosynthesis in acidic solutions of pH 1–6. Part I of this two part work addresses some of the fundamental aspects of emulsion mediation such as the composition and ionic conductivity of the organic phase, H_2O_2 partition between the aqueous and organic phases, emulsion structure, and kinetic aspects of the mediation cycle as determined by cyclic voltammetry. Furthermore, exploratory batch electrosynthesis experiments are presented.

Part II is concerned with the interactions between the electrochemical properties of the system and three-phase flow dynamics in ‘flow-by’ fixed-bed electrochemical cells.

2. Experimental details

For cyclic voltammetry experiments an Omni-90 (Cypress Systems) potentiostat was employed with the conventional three-electrode arrangement. The working electrode was a 1 mm diameter glassy carbon disc. A Pt wire functioned as the counter electrode while a mini-Ag/AgCl electrode with saturated KCl served as the

reference electrode. The working electrode was cleaned by a three-step polishing with $1 \mu\text{m}$ and $0.25 \mu\text{m}$ diamond paste and $0.03 \mu\text{m}$ alumina paste followed by sonication in methanol and double distilled water. The voltammetry experiments were performed at 295 K.

For voltammetric studies of the aprotic organic media, a bed of oven-dry molecular sieves (Davison® type 3A, Fisher Scientific) was added to the glass cell of the voltammetric equipment to minimize the water content of the solvent. In the case of the protic organic phase on the other hand, the aqueous (0.1 M H_2SO_4) and organic phases in a 1/1 volume ratio were brought into contact by purging N_2 for about 30 min. Afterwards, the two phases were left to separate and the cyclic voltammogram of the organic (i.e., top) layer was recorded under N_2 atmosphere.

To study the effect of O_2 on the voltammetric behaviour of the redox catalyst O_2 was purged at 0.1 MPa in the previously deoxygenated solution for certain time periods and the voltammogram was recorded under O_2 atmosphere. The composition of the organic phase is discussed in Section 3.1.

The H_2O_2 partition coefficient between the aqueous and organic phases was determined at 300 K for three different total H_2O_2 concentrations: 0.59, 1.2 and 1.6 M, respectively. To obtain the desired total peroxide concentration per emulsion a H_2O_2 stock solution of 0.9 M concentration was added to the emulsion composed of a 3/1 volume ratio of 0.1 M H_2SO_4 and organic phase. The emulsion, containing H_2O_2 , was mixed for 10 min to achieve equilibrium peroxide distribution between the two phases. Next, the two phases were separated in a gravity-settling funnel, samples were taken from the acid aqueous phase and analysed for peroxide content by permanganate titration. The H_2O_2 partition coefficient was calculated by a material balance.

The ionic conductivities of both aqueous and organic electrolytes were measured using a Jenway® 4020 conductivity meter equipped with a Pt conductivity cell (cell constant 1.0). The conductivity meter and cell were calibrated against two commercial standard conductivity solutions (Myron L), TDS 442-15 ($23.4 \times 10^{-4} \text{ S m}^{-1}$ at 293 K) and TDS 442-30 ($46.7 \times 10^{-4} \text{ S m}^{-1}$ at 293 K), respectively.

For preparative electrogeneration of H_2O_2 a batch glass H-cell (150 ml total volume) was used (Figure 2). Reticulated vitreous carbon served as cathode (10 cm^2 exposed geometric area $4.25 \text{ cm height} \times 2.35 \text{ cm width}$, thickness 1.3 cm). A stainless steel (316) cap and rod acted as current feeder. The catholyte was composed of various organic/aqueous acidic emulsions mixed by a magnetic stirrer under continuous O_2 purge at atmospheric pressure. A Pt cylindrical mesh with a geometric area of 24 cm^2 ($5 \text{ cm height} \times 0.75 \text{ cm width}$) immersed in 0.5 M H_2SO_4 served as anode. The anode and cathode compartments were separated by a Nafion® 117 cation exchange membrane. A saturated calomel electrode (SCE) was employed as reference electrode for the

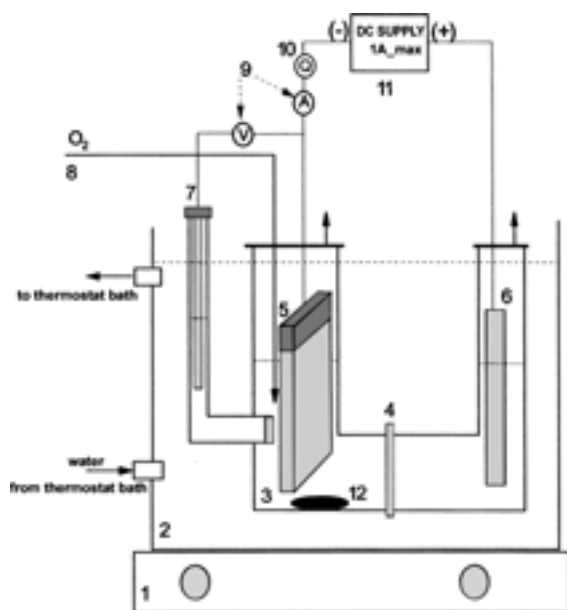


Fig. 2. Set-up and components of the H-cell. Legend: (1) mixing plate, (2) water bath, (3) glass H-cell, (4) Nafion[®] 117, (5) RVC cathode with current feeder, (6) Pt mesh anode, (7) reference electrode (SCE), (8) gas inlet, (9) digital multimeters, (10) digital coulometer, (11) d.c. power supply, and (12) magnetic stir bar.

cathode. The porous frit tip of the reference electrode compartment protruded to about 4 mm away from the back of the RVC cathode. For consistency with the voltammetry studies the cathode potentials during electrosynthesis are reported versus the Ag/AgCl, satd. KCl reference.

Current to the cell was supplied by a d.c. power supply (Anatek) with a maximum output of 1 A and 50 V. The highest current applied to the cell was 0.8 A. The cathodic current and potential were each monitored with digital multimeters, while the quantity of electricity passed through the cell was measured with a digital coulometer (model 379 PAR). The temperature was kept constant during electrolysis at 300 ± 3 K by placing the H-cell in a water bath connected to a circulating thermostat cooling bath.

At certain time intervals during electrosynthesis typically a 0.5 ml emulsion sample was withdrawn from the batch cell and the H_2O_2 content of the emulsion mixture was determined by titration with KMnO_4 .

3. Results and discussion

3.1. Composition of the organic media

The composition of the organic media plays an important role in emulsion electrosynthesis in general. For the particular case discussed here the organic phase has to meet the following criteria: low environmental hazard, good electrochemical stability, low water solubility, low peroxide retention and properties that promote current distribution at the organic phase/electrode interface.

Regarding the latter aspect, Wendt and collaborators, studying the charge transfer at the three-phase boundary (solid/organic/aqueous) involving oil-in-water (O/W) emulsions, suggested two main conditions that could assure a favorable current distribution in the organic phase. These are: enhanced ionic conductivity of the organic phase due to the presence of a lipophilic supporting electrolyte and reduced solid/organic contact angle (i.e., improved surface wetting by the organic phase) achieved by the addition of a surfactant [18–20].

Following the above recommendations, the organic phase of the present work was composed of tributylphosphate solvent (TBP, $(n\text{-C}_4\text{H}_9\text{O})_3\text{PO}$) with various concentrations of tetrabutylammonium perchlorate (TBAP, $(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{ClO}_4^-$), tricaprilmethylammonium chloride (A336[®], $(n\text{-C}_8\text{H}_{17})_3\text{CH}_3\text{N}^+\text{Cl}^-$) and 2-ethyl-9, 10-anthraquinone (EtAQ) dissolved in it, acting respectively as supporting electrolyte, cationic surfactant and redox catalyst. The cationic surfactant A336 was selected based on its effect on O_2 electroreduction to H_2O_2 induced by surface film formation [3].

First an exploratory electrosynthesis experiment was performed to compare the performance of the proposed organic system containing quaternary ammonium ions (TBP–TBAP 0.2 M–A336 0.06 M) with the emulsion used previously in the literature composed of diethylbenzene (DEB, 85% by vol.) and TBP (15% by vol.) without quaternary ammonium ions [13–15]. The electrochemical mediator for both cases was EtAQ, at 0.1 M concentration in the TBP–TBAP–A336 mixture and 0.42 M concentration in DEB–TBP. The aqueous phase was 0.1 M H_2SO_4 , with a 3/1, aqueous/organic volume ratio. Oxygen was purged continuously at atmospheric pressure.

Figure 3 shows the peroxide concentrations in the emulsion and representative current efficiencies obtained using a 39 pores per cm RVC cathode at 300 A m^{-2} .

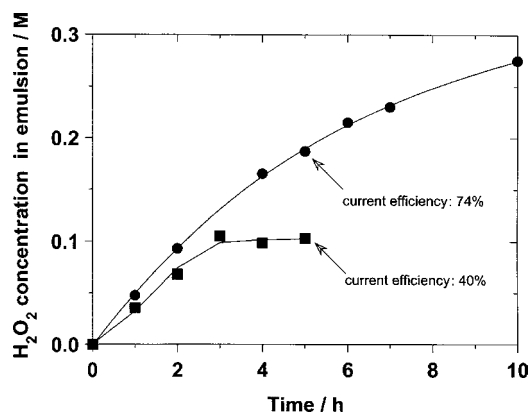


Fig. 3. Comparison between two organic phases for mediated H_2O_2 electrosynthesis using 0.1 M H_2SO_4 as aqueous phase. Cathode: RVC 39 ppc. 300 A m^{-2} , 300 K, O_2 0.1 M Pa. Legend: (●) tributylphosphate (TBP)–tetrabutylammonium perchlorate (TBAP) 0.2 M–tricaprilmethylammonium chloride (A336) 0.06 M–2-ethylanthraquinone (EtAQ) 0.1 M; (■) diethylbenzene (DEB)–TBP–EtAQ 0.42 M.

Despite a fourfold lower mediator concentration the H_2O_2 current efficiency was higher in the quaternary ammonium ions (QUAT) supported system than in the DEB–TBP mixture. In the QUAT system peroxide accumulated throughout the run to reach 0.27 M at 10 h, whereas in the DEB–TBP mixture the H_2O_2 levelled off at 0.1 M after 3 h. The cathode potentials after 2 h at 300 A m^{-2} in the QUAT system and DEB–TBP mixture were, respectively, -1.5 and below -2 V vs Ag/AgCl . At the latter potential the accumulation of peroxide is stopped by its destruction in the secondary cathode reaction (Reaction 3, Figure 1).

3.2. Determination of the H_2O_2 aqueous/organic partition coefficient

An important aspect of the present emulsion mediated electrosynthesis, although previously neglected in the literature, relates to the H_2O_2 partition between the aqueous and organic phases, that is, $K_{\text{H}_2\text{O}_2}$ defined by Equation 5:

$$K_{\text{H}_2\text{O}_2} = \frac{C_{\text{aq},\text{H}_2\text{O}_2}}{C_{\text{org},\text{H}_2\text{O}_2}} \quad (5)$$

where $C_{\text{aq},\text{H}_2\text{O}_2}$ and $C_{\text{org},\text{H}_2\text{O}_2}$ are the peroxide concentrations in the aqueous and organic phases, respectively.

Figure 4 shows $K_{\text{H}_2\text{O}_2}$ at three different total peroxide concentrations for partition between 0.1 M H_2SO_4 and two organic solvents of interest, that is, TBP and DEB (85% by vol.)–TBP (15% by vol.) mixture at 300 K.

In the case of TBP, $K_{\text{H}_2\text{O}_2}$ was fairly constant, between 1.4 and 1.5, over the range of investigated peroxide concentrations (i.e., 0.59–1.6 M H_2O_2). For the DEB–TBP mixture however, $K_{\text{H}_2\text{O}_2}$ decreased with increasing H_2O_2 concentration in the emulsion (Figure 4). Below about 1.2 M H_2O_2 , $K_{\text{H}_2\text{O}_2}$ was higher in the DEB–TBP mixture than for TBP alone, due to the presence of the nonpolar DEB (dipole moment 0.4 D [21]) inducing the

rejection of the polar H_2O_2 molecule (dipole moment 2.2 D [21]). At 1.6 M H_2O_2 in emulsion on the other hand, the partition coefficient for the mixture with DEB was lower than for TBP alone, that is, 1 and 1.5, respectively (Figure 4). This is typically due to the association of solute molecules in the organic solvent [22]. At high peroxide concentrations, it is plausible to assume that H_2O_2 molecules are able to increase their solubility in DEB by forming molecular associations with reduced overall permanent dipole.

Therefore, from the point of view electrosynthesis, at peroxide concentrations in emulsion greater than 1.2 M, the presence of DEB in the organic solvent mixture would be undesirable since it would lower $K_{\text{H}_2\text{O}_2}$. Furthermore, in assessing the potential for industrial scale use of DEB for electrochemical synthesis of peroxide, one must take into account that DEB is not expected to biodegrade, it is toxic to aquatic organisms and it presents a serious fire and explosion hazard [23]. These properties are in contrast to those of TBP [24].

Based on the above results the organic media composed of TBP–TBAP–A336 was used in subsequent studies.

3.3. Ionic conductivity and emulsion type

For electrochemical processing of organic compounds in emulsions, ideally, the electric conductivity of the organic phase should be the same order of magnitude as the conductivity of the aqueous electrolyte (e.g., $>1 \text{ S m}^{-1}$). This would reduce the overall energy requirement of the process and favour the passage of current through the organic phase, yielding a higher current efficiency.

In the present system, the dielectric constant of TBP is about 8 [21] and by itself is virtually electrically nonconductive. However, as shown by Figure 5, both TBAP and A336 impart electrical conductivity to TBP solutions.

Figure 5 (inset) shows that A336 brought about only a small increase in conductivity, that is, up to $4.8 \times 10^{-4} \text{ S m}^{-1}$ for 0.06 M A336 at 295 K. The most

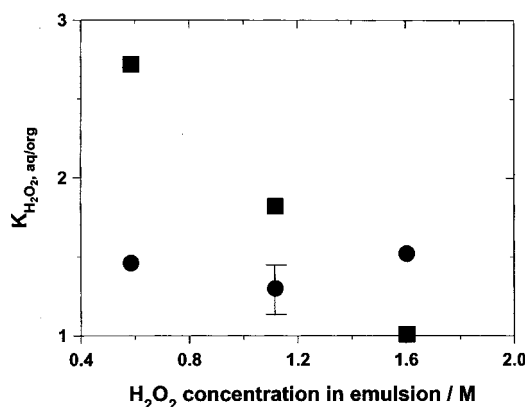


Fig. 4. The aqueous/organic partition coefficient of H_2O_2 as a function of the total H_2O_2 concentration in emulsion. Aqueous phase: 0.1 M H_2SO_4 . Aqueous/organic phase volume ratio: 3/1. 300 K. Legend: organic phase (●) TBP and (■) DEB–TBP mixture.

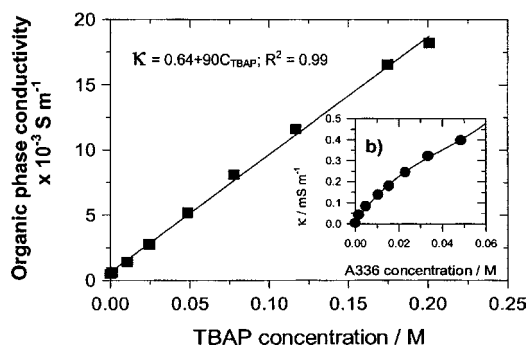


Fig. 5. Organic phase conductivity as a function of supporting electrolyte (TBAP) and cationic surfactant (A336) concentration (inside figure) 295 K.

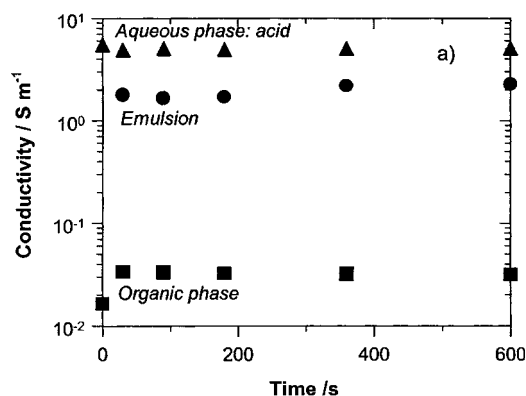


Fig. 6. Ionic conductivity of the emulsion electrolyte and its components, 295 K.

important contribution to the organic phase conductivity is due to TBAP. For the investigated range of TBAP concentrations (i.e., up to 0.2 M which is near the solubility limit in TBP at 295 K), the conductivity increased linearly from $4.8 \times 10^{-4} \text{ S m}^{-1}$ (with 0.06 M A336 present only) to 0.018 S m^{-1} (Figure 5).

In addition to the conductivity of the organic phase, it is of interest to determine the conductivity of the emulsion. The conductivity measurement could also reveal the emulsion type, which can have significant implications on the multiphase peroxide electrosynthesis.

The emulsion was composed of a 3/1 volume ratio of aqueous and organic phases. The former being 0.1 M H_2SO_4 while the organic phase was a mixture of TBP–0.2 M TBAP–0.06 M A336–0.1 M EtAQ. The two phases were mixed for 10 min at 295 K and the conductivities of the emulsion, aqueous and organic phases were determined intermittently (Figure 6).

Figure 6 shows that during the first 30 s of emulsification the conductivity of the organic phase increased from 0.016 to 0.032 S m^{-1} due to the slight solubility of water in TBP (i.e., 0.6% by vol. at 293 K [25]). After the first few minutes of mixing however, the conductivity of the emulsion and the component phases, aqueous and organic, levelled off at 2.3, 5.1 and 0.032 S m^{-1} , respectively (Figure 6).

Regarding the emulsion structure, based on the phase volume ratio assuming an oil-in-water (O/W) emulsion, the conductivity should respect the Maxwell formulae given by Equation 6 [26]:

$$\frac{\kappa_{\text{em}}}{\kappa_{\text{aq}}} = \frac{\kappa_{\text{org}} + 2\kappa_{\text{aq}} - 2\varepsilon(\kappa_{\text{aq}} - \kappa_{\text{org}})}{\kappa_{\text{org}} + 2\kappa_{\text{aq}} + \varepsilon(\kappa_{\text{aq}} - \kappa_{\text{org}})} \quad (6)$$

where κ_{em} , κ_{aq} and κ_{org} conductivity of the emulsion, aqueous and organic phase (S m^{-1}), respectively, and ε volume fraction of the organic (dispersed) phase.

Substituting into Equation 6 the aqueous and organic phase conductivity values from Figure 6 (i.e., 5.1 and 0.032 S m^{-1}) one obtains an emulsion conductivity κ_{em} , of 3.4 S m^{-1} . The measured emulsion conductivity, on

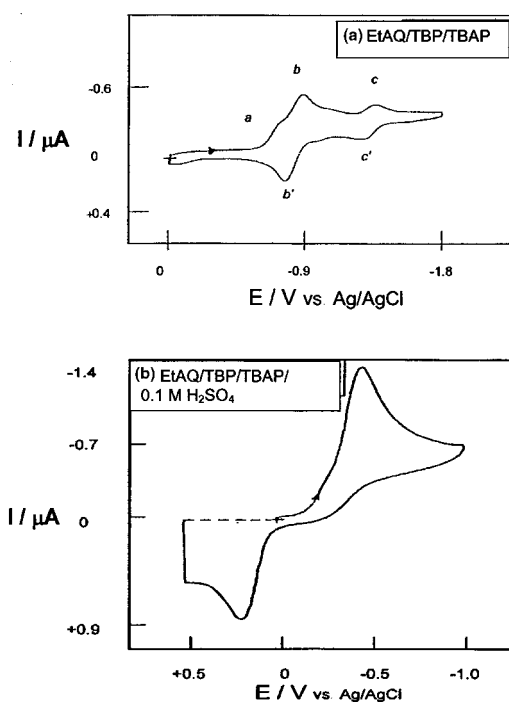


Fig. 7. Cyclic voltammetry of 2-ethylanthraquinone on glassy carbon. EtAQ concentration $1.1 \times 10^{-3} \text{ M}$. Legend: (a) aprotic conditions (TBP–0.1 M TBAP– $9.6 \times 10^{-3} \text{ M}$ A336), scan rate 0.02 V s^{-1} , (b) protic conditions: same organic phase as above in contact with 0.1 M H_2SO_4 , scan rate 0.1 V s^{-1} , 295 K.

the other hand, was 32% lower, that is, 2.3 S m^{-1} (Figure 6). Clearly, the aqueous continuum–organic dispersed (i.e., O/W) model does not fit the experimental data. Since the emulsion conductivity is close to the average conductivity between the two phases, a dual (or possibly bicontinuous) emulsion structure is proposed. The physical model of a dual emulsion involves an enclosed aqueous phase within organic droplets dispersed in an aqueous continuum, that is, W/O/W [27]. Furthermore, the surfactant architecture number of one for A336 [11] indicates a preference for bilayer arrangement of surfactant molecules at the aqueous/organic interface, leading potentially to bicontinuous emulsification and liquid membrane formation [28].

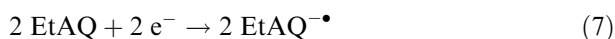
3.4. Kinetic aspects of redox catalysis

An important issue that had to be addressed in the cyclic voltammetry study was the effect of the aqueous phase (i.e., proton source, 0.1 M H_2SO_4) and O_2 on the electrochemical behaviour of EtAQ from the organic phase.

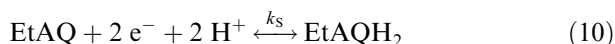
Figure 7 shows the cyclic voltammogram of 10^{-3} M EtAQ dissolved in a deoxygenated TBP–0.1 M TBAP–0.01 M A336 mixture. The voltammogram in Figure 7(a) was obtained in the absence of proton source, while Figure 7(b) shows the effect of 0.1 M H_2SO_4 on the electrochemical behaviour of EtAQ from the organic layer after a 30 min mixing period of the two phases under N_2 purging.

In the absence of acid, Figure 7(a), two peaks, denoted *b* and *c*, are observed on both the cathodic and anodic scan. These peaks are well documented in the literature [29] and they belong to the EtAQ/EtAQ^{•-} and EtAQ^{•-}/EtAQ²⁻ couples, with cathodic peak potentials at -0.86 V and -1.38 V vs Ag/AgCl, respectively. The large separation between the two peaks is an indication of the stability of EtAQ^{•-} radical-anion in the presence of quaternary ammonium ions supporting electrolyte.

With the proton source present, the electrochemical behaviour of EtAQ is altered significantly (Figure 7(b)). Only one peak is obtained on both scans, characterized by a cathodic peak potential of -0.44 V and an anodic peak potential at +0.2 V. The latter potential is typical for the oxidation of the fully protonated quinone dianions [30], that is, EtAQH₂ in the present case. The absence of a second peak when the organic phase is in contact with acid is most likely due to the fast disappearance of EtAQ^{•-} through protonation followed by disproportionation of EtAQH[•] according to the sequence of Equations 7–9 [9, 29–31]:



Thus, based on the cyclic voltammogram the overall mechanism for EtAQ electroreduction in the case of acid emulsion is quasi-reversible involving a two-electron two-proton transfer:



The proposed mechanism suggests that the reaction zone for EtAQ electroreduction in acid emulsion must be located at the proton-rich, solid/organic/aqueous boundary. This conclusion was corroborated by spectrophotometric observations on the development of the reaction front in a deoxygenated emulsion [11].

When O₂ was purged into a previously deoxygenated electrolyte (Figure 8), after about 15 s of purge the cathodic peak current doubled in comparison to the case without O₂ (Figure 8(a)). On the other hand, the anodic peak current at a potential of +0.2 V vs Ag/AgCl diminished as a result of the consumption of EtAQH₂ in the chemical reaction with O₂. After a longer period of O₂ purge (e.g., 15 min) the anodic peak can no longer be detected, indicating that EtAQH₂ is consumed completely in the reaction with O₂. Furthermore, on the cathodic scan two waves can be distinguished, that is, a sigmoid response with a half-wave potential of -0.5 V followed by a peak at -1.3 V vs Ag/AgCl. The latter belongs to the direct 2 e⁻ O₂ reduction in the protic TBP [11], while the sigmoid wave is due to the redox regenerated EtAQ electroreduction.

Based on Figure 8 it can be inferred that the rate of reaction between O₂ and EtAQH₂ is fast since the

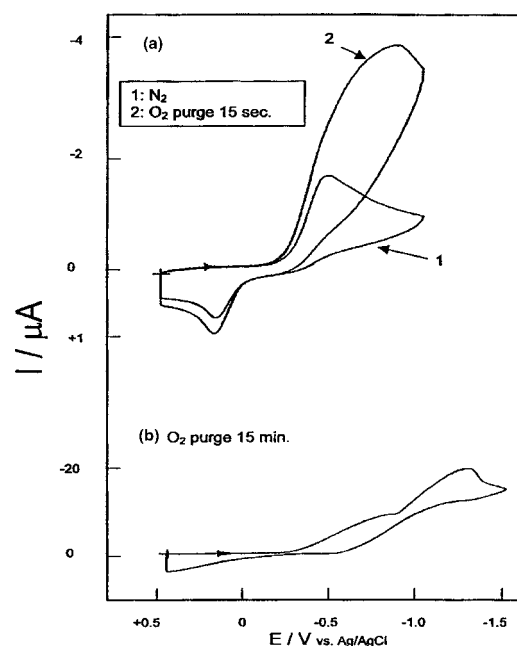


Fig. 8. Effect of O₂ at 0.1 MPa on the 2-ethylanthraquinone cyclic voltammogram on glassy carbon under protic conditions. Legend: (a) 1 N₂ purge, 2 O₂ purge for 15 s, (b) O₂ purge for 15 min. Scan rate 0.1 V s⁻¹, 295 K.

anodic peak is absent in the O₂ enriched solution. However, an assessment of the homogeneous oxidation rate constant *k_C* is needed. Using the cyclic voltammetry data, an apparent first-order rate constant *k_C* of 0.11 s⁻¹ was obtained (Appendix 1).

The intrinsic kinetic rates of the homogeneous oxidation reaction, with *k_C* equal to 0.11 s⁻¹, and that of EtAQ electroreduction will both affect the H₂O₂ production rate. Generally, the kinetic parameters for the electroreduction of quinones are sensitive to electrolyte composition, electrode material and quinone structure [32, 33].

It must be noted that the real case scenario in an electrosynthesis reactor is more complex involving mass transfer effects associated with the multiphase system and side reactions such as H₂ evolution and/or H₂O₂ electroreduction.

3.5. Batch electrosynthesis

Exploratory peroxide electrosynthesis experiments were performed in an H-cell with an RVC cathode of 12 pores per cm, specific surface area 1800 m² m⁻³ [34]. Superficial current densities between 500 and 800 A m⁻² were employed. The catholyte was a 3/1 volume ratio of aqueous acidic to organic phase. The organic phase contained 0.2 M TBAP, 0.004–0.06 M A336 and 0.1–0.2 M EtAQ. Oxygen was purged at atmospheric pressure over the entire 10 h experiment. The temperature was 303 K.

Figure 9 compares the performance of the redox catalysed system with that of direct O₂ electroreduction in the presence of 10⁻³ M A336. At 500 A m⁻² the latter

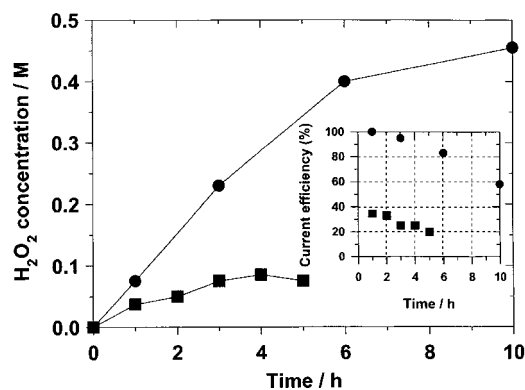


Fig. 9. Comparison between mediated and direct O_2 electroreduction to H_2O_2 . Cathode RVC 12 ppc, 500 A m^{-2} , 303 K, O_2 0.1 MPa. Legend: (●) mediated organic phase TBP–0.2 M TBAP–0.1 M EtAQ, aqueous phase 0.1 M H_2SO_4 , phase volume ratio: 3/1_{aq/org}, 10^{-3} M A336 per emulsion; (■) direct O_2 reduction in 0.1 M H_2SO_4 with 10^{-3} M A336 present.

method gave a maximum H_2O_2 concentration in 0.1 M H_2SO_4 of 0.09 M, corresponding to 25% current efficiency. With redox catalysis on the other hand the H_2O_2 concentration increased over a 10 h period, yielding 0.46 M H_2O_2 (per emulsion) with 55% current efficiency. At 500 A m^{-2} the cathode potential for the O_2 /A336 system was between -1.9 and -2.6 V vs Ag/AgCl where the secondary electrode reactions such as H_2O_2 reduction and H_2 evolution gain significance, and lower the efficiency of peroxide production. In the case of redox catalysis on the other hand, the cathode potential over the 10 h period was between -1.3 and -1.7 V vs Ag/AgCl. These results show clearly the importance of EtAQ redox catalysis relative to direct O_2 electroreduction for H_2O_2 synthesis in acid media.

The effect of cationic surfactant (A336) concentration on the emulsion mediated electrosynthesis at 500 A m^{-2} , was also investigated. Figure 10 shows that generally increasing the A336 concentration increased the peroxide concentration and current efficiency after the first three hours of the experimental run. In the absence of

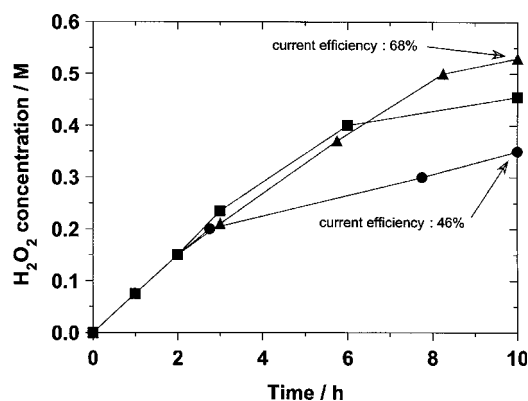


Fig. 10. Effect of cationic surfactant (A336) concentration on the performance of mediated H_2O_2 electrosynthesis. Cathode RVC 12 ppc, 500 A m^{-2} , 303 K, O_2 0.1 MPa. Aqueous phase 0.1 M H_2SO_4 . Organic phase TBP–0.2 M TBAP–0.1 M EtAQ. Phase volume ratio: 3/1_{aq/org}. Legend: A336 concentration (M) per emulsion (●) 0, (■) 10^{-3} and (▲) 1.5×10^{-3} .

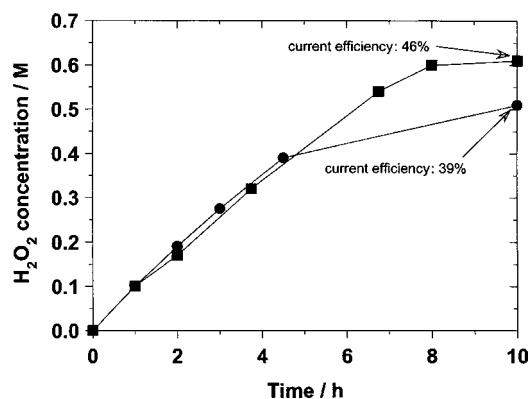


Fig. 11. Effect of mediator concentration on H_2O_2 electrosynthesis using 2 M Na_2SO_4 aqueous phase at pH 3. Cathode RVC 12 ppc, 800 A m^{-2} , 303 K, O_2 0.1 MPa. Organic phase TBP–0.2 M TBAP–0.1 M EtAQ–0.06 M A336. Phase volume ratio: 3/1_{aq/org}. Legend: 2-ethylanthraquinone concentration (M) (●) 0.1 and (■) 0.2.

surfactant, after 10 h 0.36 M H_2O_2 was obtained. However, with 0.015 M A336 per emulsion (i.e., 0.06 M A336 added to the organic phase) the H_2O_2 concentration in the cell after 10 h was 0.53 M, corresponding to an apparent current efficiency of 68%. The effect of the A336 is most likely due to a combination of several factors such as improved wetting of the cathode surface by the organic phase and an influence on both O_2 and H_2O_2 electroreduction kinetics [3, 11]. Regarding the latter reaction it was found that mM concentrations of A366 dispersed in 0.1 M H_2SO_4 diminished the rate of H_2O_2 electroreduction on RVC cathodes [11].

In addition to 0.1 M H_2SO_4 aqueous phase, exploratory experiments were performed using an aqueous electrolyte composed of 2 M Na_2SO_4 acidified with glacial acetic acid to an initial pH of 3. This solution could be relevant for certain acidic peroxide wood pulp bleaching methods such as the GreenOx[®] process [12]. Figure 11 shows the H_2O_2 concentration in emulsion as a function of EtAQ concentration, obtained after 10 h of electrolysis using the 12 pores per cm RVC cathode operated at 800 A m^{-2} superficial current density. With 0.2 M EtAQ dissolved in the organic phase (i.e., near the solubility limit in TBP at 295 K) a H_2O_2 concentration of 0.61 M was obtained after 10 h (apparent current efficiency 46%). As expected the pH of the catholyte increased during the 10 h electrolysis. The final pH of the aqueous phase was between 5 and 5.7, which is adequate for acidic peroxide bleaching [12].

4. Conclusions

The EtAQ redox catalysed (or mediated) H_2O_2 electrosynthesis was investigated in acidic solutions using a three-phase, aqueous/organic/gaseous system. It was found that the presence of quaternary ammonium ions, acting as organic supporting electrolyte (i.e., TBA) and cationic surfactant (i.e., A336) respectively, is essential for satisfactory figures of merit, such as peroxide concentration and current efficiency. A comparative

experiment carried out in the absence of quaternary ammonium ions but with fourfold higher mediator (EtAQ) concentration, yielded H_2O_2 concentrations approximately three times lower than with quaternary ammonium ions present in the organic phase.

Conductivity measurements were used to determine the emulsion structure. For an emulsion composed of a 3/1 volume ratio of 0.1 M H_2SO_4 and organic phase (i.e., TBP–0.2 M TBAP–0.06 M A336–0.1 M EtAQ), dual (or bicontinuous) emulsion structure was observed.

Cyclic voltammetry studies revealed an overall two-electron, two-proton mechanism for EtAQ electroreduction in the acid emulsion. The homogeneous first-order rate constant for the EtAQH₂ reaction with dissolved O_2 was determined from cyclic voltammetry studies as 0.11 s^{-1} .

Batch electrolysis experiments showed the possibility of mediated H_2O_2 electrosynthesis in acidic solutions ($\text{pH}_{\text{initial}}$ 0.9 and 3, respectively) at superficial current densities of 500 and 800 A m^{-2} using reticulated vitreous carbon cathodes of 12 pores per cm. During the 10 h batch electrolysis, peroxide concentrations up to the range 0.53–0.61 M were obtained. These results warranted further investigations of the quaternary ammonium ion supported system under conditions closer to potential industrial applications. In this regard, experimental results obtained with flow-by fixed-bed electrochemical cells operated with co-current upward L/L/G flow are reported in Part II of this communication.

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Appendix 1: Calculation of the apparent first order homogeneous rate constant k_C for the EtAQH₂– O_2 reaction

From cyclic voltammetry theory [35] it is known that the ratio of redox regenerated limiting current $I_{L,R}$ (i.e., corresponding to EtAQ electroreduction in the presence of O_2) to the peak current in the absence of redox regeneration $I_{p,c}$ (i.e., EtAQ reduction in N_2 saturated electrolyte) is related to the apparent homogeneous rate constant of EtAQH₂ oxidation k_C according to Equation A1:

$$\frac{I_{L,R}}{I_{p,c}} = 2.242 \left(\frac{RT}{nF} \times \frac{k_C}{v} \right)^{1/2} \quad (\text{A1})$$

where v is the scan rate (V s^{-1}), F the faradaic constant, n the total number of electrons, R the universal gas constant and T the temperature.

Substituting the cathodic currents corresponding to cyclic voltammograms similar to those given by Figure 8 but obtained at scan rates between 2×10^{-3} and 10^{-2} V s^{-1} [11], from Equation A1 an average k_C value of 0.11 s^{-1} was obtained.